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C—2—3 Characterization of Computer Controlled GaP Single Crystals

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Computer controlled liquid encapsulated Czochralski (C-LEC) growth[1] has accomplished the quality improvement of gallium phosphide (GaP) single crystals, in addition to perform the automatic diameter control and to improve the growth reproducibility. High performance green and yellow light emitting diodes (LEDs) were obtained by using the large diameter (2～2.5"ϕ) ⟨111⟩ and ⟨100⟩ oriented GaP crystals grown by C-LEC method. This paper is concerned with the detailed characterization of the C-LEC ⟨111⟩ and ⟨100⟩ crystals, as compared with that of the commercially available crystals.

C-LEC growth has enabled automatic diameter control with reasonably good diameter control without a "coracle" [2] which is a floating diameter-defining aperture made from Si_3N_4 and is used for diameter control of commercially available ⟨111⟩ GaP crystals. C-LEC method can suppress contamination by impurities and void appearance which are frequently observed in the coracle crystals. Table I shows the results of mass spectrometric analysis for the C-LEC crystals and the coracle crystals. The C-LEC crystals are superior in purity; especially in silicon contamination. Figure 1 shows the Hall mobility as a function of the electron concentration for the C-LEC and coracle crystals. Dash lines in Fig. 1 are the calculated curves for various values of compensation ratio (N_A/N_D). Figure 1 indicates that the C-LEC crystals have about 10% higher Hall mobility than that of the coracle crystals and have lower compensation ratios of 0.2～0.5. Influence of impurity on crystal quality will be discussed in detail.

All C-LEC crystals included no macroscopic defects such as impurity precipitates and voids. Figure 2 shows a typical void observed in the coracle crystal. These voids contained inclusions which were composed of silicon, boron, oxygen and phosphorus. The green electroluminescence emission efficiency of GaP:N epitaxial layer using (111) substrate containing above voids was very low at and near the voids. On the other hand, brightness uniformity was obtained in the 2" diameter epitaxial layer using the C-LEC crystals.

Commercially available ⟨100⟩ oriented GaP single crystals for yellow and orange LEDs have been grown without a coracle due to a higher propensity for twinning using the coracle method. C-LEC method has enabled automatic diameter control without a coracle even in the lower temperature gradient in which manual growth is more difficult with diameter control. Growth in the lower temperature gradient results in lowering a dislocation density. Figure 3 shows typical preferential R-C etching patterns on (100) plane for the C-LEC ⟨100⟩ crystal and the commercially available one. A less than $5 \times 10^4\ cm^{-2}$ dislocation density has been obtained for the both C-LEC ⟨111⟩ and ⟨100⟩ crystals which have been grown in the lower temperature gradient than 70 °C/cm. But the commercially available ⟨100⟩ crystals have higher dislocation density than 1 x 10^5 cm^{-2} due to manual growth in the higher temperature gradient. The yellow LEDs using the C-LEC crystals having a low dislocation density showed extreamely high external quantum efficiency, 0.3%, which was about 2～3 times higher than that of LEDs using the commercially available ⟨100⟩ crystals.

References

1) T.Fukuda, S.Washizuka, Y.Kokubun, J.Ushizawa and M.Watanabe : to be published in Proc. 1981 Int. symp. GaAs and Related Compounds.

2) R.M.Ware and M.Whitaker : The 5th International Conference on Crystal Growth, Abstract 132, 1977, Boston, U.S.A.

Table I. Results of mass spectrometric analysis. (ppm)

	Fe	Cu	Zn	Cr	Ca	K	Cl	Si	Al	Mg	Na	B
C-LEC crystals	0.4	0.16	0.1	0.02	0.8	0.4	0.3	3.4	0.5	0.06	0.7	0.02
Coracle controlled crystal	1.6	0.2	0.2	0.04	4.0	1.7	1.2	26	3.6	0.2	3.5	0.5

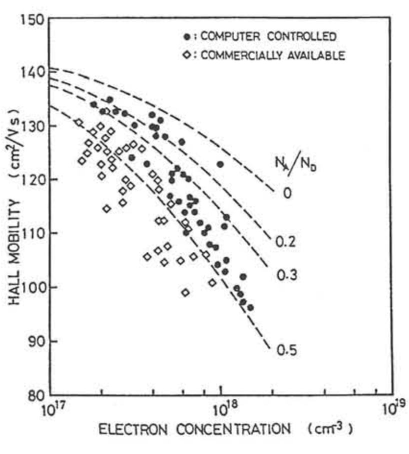
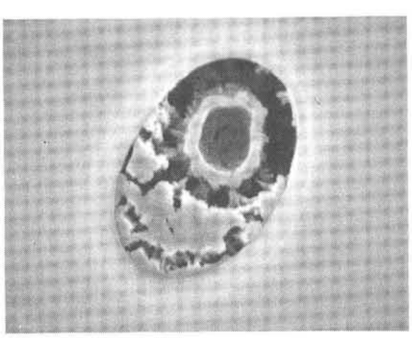
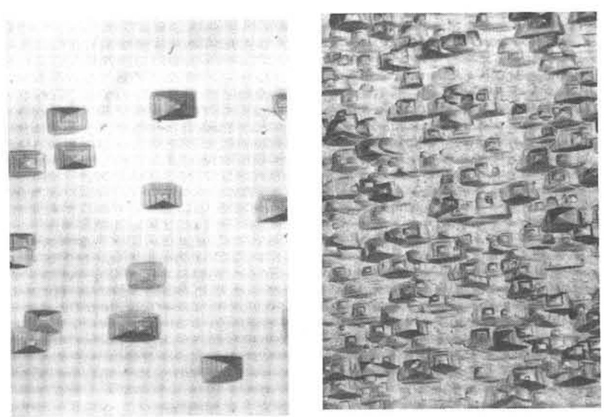


Fig. 1. Hall mobility as a function of electron concentration.



1 μ

Fig. 2. A typical void with inclusions.



(a) 50μ (b)

Fig. 3. Typical (100) plane etching patterns.

(a) For a computer controlled crystal

(b) For a commercially available crystal